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A. O. Mattheus

The Oxidation of Azo Compounds to  
Azoxo Compounds



THE OXIDATION OF AZO COMPOUNDS TO AZOXY  
COMPOUNDS BY MEANS OF ACYL HYDROPEROXIDES

BY

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B. S. University of Illinois, 1918

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

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MASTER OF SCIENCE

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY ALBERT OTTO MATTHEUS

ENTITLED THE OXIDATION OF AZO COMPOUNDS TO AZOXY

COMPOUNDS BY MEANS OF ACYL HYDROPEROXIDES

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR  
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## INTRODUCTION I

The work presented in this dissertation concerns itself primarily with the oxidation of the azo compounds to the azoxy compounds by means of acetyl hydro peroxides and it shows in some specific instances the value of these hydro peroxides as oxidizing agents for compounds containing the N:N linkage. It brings put experimental evidence in favor of the hypothesis presented at the beginning of the present century by a eminent chemist concerning the structure of the azoxy compounds.



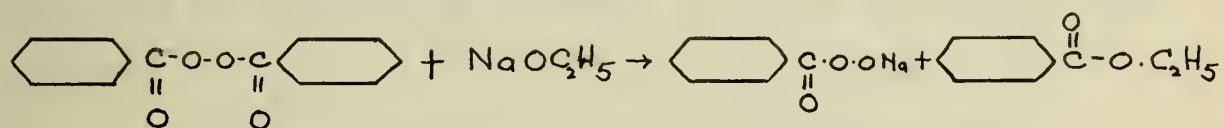
## HISTORICAL II

The organic peracids can be considered as derivatives of hydrogen peroxide in which one of the hydrogen atoms of the peroxide has been replaced by an aromatic or aliphatic acid residue. For a long time the best methods available for the preparation of these peracids involved reactions in which the organic peroxides were first formed and then decomposed by suitable reagents with the formation of the peracids.<sup>1</sup> This decomposition reaction was applicable in only a limited number of cases, not<sup>at</sup> all however, with the alkyl hydroperoxides. Although the existence of peracids as the intermediate products in the auto oxidation of the aldehydes had been known, the above method involving the splitting of the organic peroxides was the only one available. Peroxides of the acyl type were first prepared by Brodie,<sup>2</sup> who, by the action of barium peroxide on acetic anhydride, the former being gradually added to the cold ethereal solution of the latter, succeeded in preparing acetyl peroxide. The yield was poor. He describes the substance as an oil which solidifies at a low temperature, and which readily decomposes in sun-light. He found it to be an energetic oxidizing agent, liberating iodine and chlorine from hydroiodic and hydrochloric acids respectively. It does not decolorize chromic acid or potassium permanganate. Thiele and Vanino<sup>3</sup> prepared the same compound by the action of acetyl chloride on an ice cold solution of sodium peroxide and sodium acetate, however, they only had the substance in an impure state. Peroxides of fumaric, succinic, phenylacetic, and camphoric acids

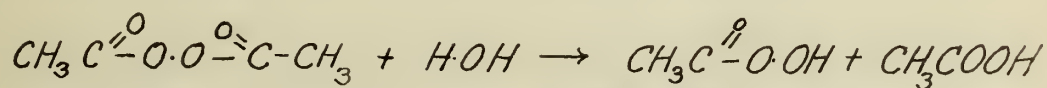




had also been prepared by a similar method. Nef<sup>4</sup> studied these substances further and found that by the action of 2 mols of acetic anhydride on one mol of hydrogen peroxide these peroxides could be formed in very good yields. Peroxides of the aryl type were prepared by Baeyer and Villiger<sup>5</sup> by similar methods, and they found that these peroxides on treatment with sodium ethylate were decomposed into the sodium salt of the per acid and the ethyl acetate of the acid. By careful acidification of the ether



with sulphuric acid the free per acid was obtained. This method of hydrolysis has only been investigated in a few cases. Cloves and Richmond studied the hydrolysis reactions of the peroxides and found that the peroxides on treatment with water liberated the peracid together with the acid corresponding to the oxide. This peracid then further reacted with the water with the formation of the simple acid and hydrogen peroxide. They were, however, unable to reverse this reaction and reform the peracid from the acid itself and the hydrogen peroxide. However,

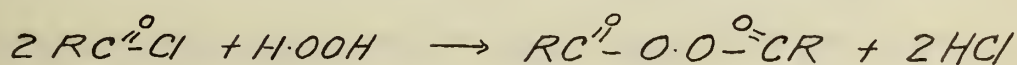
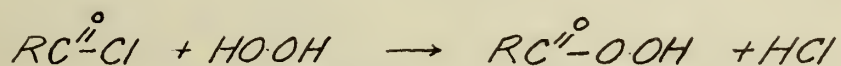


Friederich obtained traces of peracetic acid by allowing glacial acetic acid to stand with hydrogen peroxide. The reaction was very slow but he found that the rate of formation could be in-

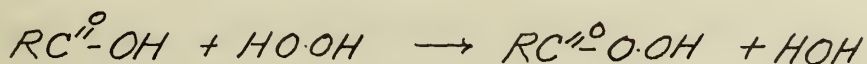
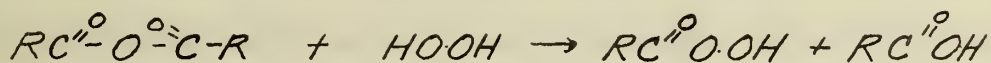




creased by using a catalyst as sulphuric acid. Later J d'Ans and W. Friederich<sup>6</sup> studied the reaction <sup>between</sup> acid chlorides and hydrogen peroxide, and in this way succeeded in preparing per sulphuric acid, by the action of chlor sulphonic acid upon hydrogen peroxide. At the same time he investigated the reaction between acid chlorides of the organic type and succeeded in preparing together with the peracid of the corresponding acids, the peroxide. The reaction consisted in the replacement of the hydrogens of the hydrogen peroxide by one or two mols of acid residue



residue. Later modifications of this reaction showed that the ~~acid~~ acid chloride could be replaced by the acid anhydride. The reaction was very successful for the preparation of the peracids in view of the fact that the final product was in most cases entirely free from the objectionable peroxides. The following is the course of the reaction:



Peroxides of the following acids were obtained: performic, peracetic, perpropionic, perbutyric. This method of preparation is unquestionably the best available for the preparation of peracids in a high state of purity.



## THEORETICAL III

Systematic attempts to apply the peracids as special oxidizing agents for some organic chemicals had been undertaken by several investigators. Prileschajew<sup>7</sup> working with benzoylhydroperoxide succeeded in carrying out oxidation of unsaturated  $-C:C-$  compounds and found that as a direct result of the oxidation an oxide ring  $\begin{array}{c} C - C \\ \backslash \quad / \\ O \end{array}$  resulted which on treatment with water in the presence of sulphuric acid opened up and gave a glycol as a final product.  $\begin{array}{c} -C - C- \\ \backslash \quad / \\ O \end{array} + HOH \quad \begin{array}{cc} -C - C- \\ | \quad | \\ OH \quad OH \end{array}$

This he succeeded in doing

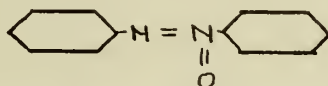
on a variety of  $-C:C-$  compounds. J d'Ans and A. Kniep<sup>8</sup> after successfully preparing peracetic acid used this reagent in a large number of oxidations. They were able to oxidize benzaldehyde to benzoic acid, anisaldehyde to anisic acid, and p-oxybenzaldehyde to p-oxybenzoic acid. They oxidized aniline to nitroso benzene and azoxybenzene, p-toluidine to nitroso toluene and azotoluene and several other substituted aniline derivatives, in each case, the nitroso compound was formed in an exceedingly large excess than the corresponding azoxy derivative. They further oxidized azobenzene to azoxybenzene, p-azotoluene to p-azoxytoluene, m-m'-dinitroazobenzene to m-m'-dinitroazoxybenzene, and p-p'-dinitroazobenzene to p-p'-dinitroazoxybenzene. Whether there are intermediate stages in the reaction the author of this work was not able to determine, but there were indications at times that such might be the case, for on several occasions the addition of the peracetic solution to the substance to be oxidized resulted in a solution of much more intense color. This color, however, disappeared at the end of 30 minutes and



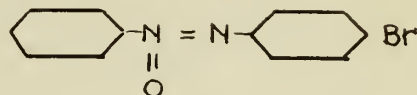
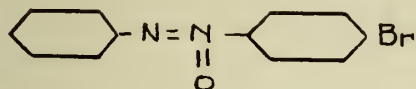


and the condition of the oxidized solution was the same as in those cases in which there was an immediate change in color intensity.

The substances which were used as a medium of testing the merits of the peracetic acid as an oxidizing agent were the unsymmetrical azobenzenes. These compounds had been prepared by Angeli<sup>9</sup> using strong hydrogen peroxide as an oxidizing agent. He thoroughly investigated the oxidation products of these compounds and accumulated evidence which seems to indicate the presence of isomeric compounds. It is evident that in the oxidation of azobenzene to azoxybenzene only one form is theoretical-



ly possible. In the case of unsymmetrical azoxybenzenes it is theoretically possible to obtain isomers and if such were true



then one of the nitrogen atoms must contain the oxygen attached with a double union.

The question which presents itself then is whether it is possible to separate two or more products from the oxidation reaction upon an unsymmetrical azobenzene and if so how can the exact identity of these compounds be established. Angeli presents evidence in the form of bromination reactions upon unsymmetrical p-bromazoxybenzene for example and shows that the ease of bromination is different with the two isomers both being subjected to the same experimental conditions. The



work which is to follow gives some evidence of the existence of such isomers, this evidence however not being conclusive proof for the existence of these isomers.





## EXPERIMENTAL IV.

## Preparation of p-Ethoxy Aniline.

Para ethoxy aniline was prepared by the hydrolysis of phenacetin according to the method of Erdmann.<sup>10</sup>

A mixture of 100 grams of phenacetin, 200 cc HCl (C.P) and 200 cc of water was refluxed in a 1000 cc round bottomed flask for one hour. To the cooled solution 400 cc of water and enough sodium hydroxide was added to insure an alkaline reaction. The brown oil was removed with a separatory funnel and the remaining alkaline solution extracted twice with ether. The ethereal extract together with the separated oil was filtered and allowed to stand over solid sodium hydroxide. After allowing to dry from 6 to 8 hours the product was distilled. At a temperature of 254-256 C the base separates as a straw colored oil. A yield of 72 grams or 82% of the theoretical yeald was obtained

## Preparation of Unsymmetrical Azobenzenes.

The preparation of unsymmetrical azobenzenes in a very high degree of purity can be carried by undergoing the following reactions:

1. Preparation of B-phenyl-hydroxylamine.
2. Oxidation of B phenyl-hydroxylamine to nitroso benzene.
3. Condensation of nitroso benzene with a para substituted aniline.



### 1. Preparation of B-Phenyl-Hydroxylamine.

One hundred and sixty-six grams of nitro benzene contained in a ten liter flask was vigorously stirred with 2560 cc of water and 84 grams of ammonium chloride. To this mixture 222 grams of zinc dust was added through a sieve during a period of 15 minutes. The temperature of the solution soon rose to 60 C and by the occasional addition of ice together with a regulated addition of zinc dust it was maintained between 55 - 60 C but at no time was it allowed to exceed 60 C. At the end of twenty minutes following the last addition of zinc dust, the solution was filtered with suction through a six inch Buchner funnel. The dry zinc oxide was then transferred to the original ten liter flask and shaken with 500 cc of warm water. This mixture was then filtered and the residue in the filter was washed with an additional 500 cc of water. To the combined filtrates, slightly yellow in color, sodium chloride was added to the point of saturation and the solution allowed to cool in a salt and ice mixture. During the cooling of the solution vigorous stirring was applied. The crystals of B-phenyl-hydroxylamine was separated by suction.

### 2. Oxidation of B-Phenyl-Hydroxylamine to Nitroso Benzene.

To a mixture of 90 grams of B-phenyl-hydroxylamine and 3500 cc of water, 1000 grams of ice and 270 grams of conc. sulphuric acid were added. A solution made by dissolving 108 grams of potassium dichromate in 5000 cc of water was cooled





by the addition of 2750 grams of ice and when there was no further drop in temperature the solution was poured as quickly as possible into the ice cold B-phenyl-hydroxylamine solution. Vigorous stirring accompanied the reaction. After a period of three-quarters of an hour the nitroso benzene was filtered off, and washed with water. The amount of ice added was sufficient to maintain a low temperature throughout the entire reaction.

In the condensation reaction of B-phenyl-hydroxylamine with an amine, a cleaner condensation product is obtained if the nitroso benzene used is purified. The purification can be very easily accomplished by steam distillation and flaky white solid is obtained.

### 3. Condensation of Nitroso Benzene with a para Substituted Aniline.<sup>11</sup>

#### Preparation of p-ethoxy-azobenzene.

Thirty grams of purified nitroso benzene, 235 grams of glacial acetic acid and 30 grams of p-ethoxy-aniline were allowed to stand in a 1000 cc round bottom flask for 12 hours. The reaction mixture was then poured into cold water and after allowing it to stand for several hours the coagulated precipitate was filtered, wash with water and dried on filter paper. The impure product was then dissolved in 800 cc of conc. hydrochloric acid and the mixture cautiously heated to 50 C. The hydrochloric acid solution was then filtered through a gooch crucible funnel containing glass wool. On cooling brick-red crystals separated from the acid solution which, after filtration and exposure to the air yielded a brownish colored product.



This brown product was then twice recrystallized from 95% alcohol and beautiful crystals of p-ethoxy-azobenzene were obtained. The crystals melted sharply at C.

This method of purification yields a much better looking and sharpening melting product than the product which is obtained by the usual method of direct crystallization of the crude condensation product from 95% alcohol.

#### Preparation of p-brom-azobenzene.

Eighty grams of p-brom-aniline (M.P. 66.4 C) was dissolved in 200 cc of glacial acetic acid and to this mixture 55 grams of purified nitroso benzene was added. In a short period of time the reaction mixture became warm and intensely dark in color. After standing for 12 hours, the reaction mixture was cooled to 15 C and the crystals which separated from the acetic acid solution were filtered off and washed with water. It has been found that if this procedure is adopted many of the impurities will remain dissolved in the acetic acid solution and the resulting azo compound obtained will be very pure. The loss due to this operation is not very large as only a small amount of the azo benzene remains in the acetic acid solution. The crude product obtained was twice recrystallized from 95% alcohol and crystals melting sharply at 88 C were obtained. A yield of 65% of the theoretical yield was obtained.

#### Preparation of p-nitro-azobenzene.

Attempts to prepare p-nitro-azobenzene by the condensation of nitrobenzene with p-nitroaniline were unsuccessful. This is of interest for it seems to indicate that only those para substituted anilines which are basic in nature are





capable of undergoing this condensation.

#### Preparation of Hydrogen Peroxide.

Hydrogen peroxide of high concentration was prepared by first distilling the three per cent commercial product under diminished pressure to a concentration of approximately 80% and then subjecting this product to a freezing mixture by means of which solid hydrogen peroxide was obtained.

The vacuum distillation system used for the concentration of the commercial product consisted of a two liter pyrex distilling flask, a 24 inch condenser, a 1000 cc receiver, a manometer, and electrically driven oil vacuum pump. A suction flask containing acidulated potassium permanganate was placed between the manometer and the pump, to act as a trap for hydrogen peroxide, thus protecting the pump from too rapid deterioration. The pyrex distilling flask was provided with a few glass beads to prevent bumping and a capillary tube leading to the bottom of the flask for the introduction of air. A pan filled with water and heated with a bunsen burner was used to supply the necessary heat for the distillation process. In order to avoid an possibility of super heating<sup>of</sup> the distillation flask, a cork ring, upon which the distillation flask rested was placed in the bottom of the pan.

The starting material consisting of commercial three per cent hydrogen peroxide, previously filtered to remove any solid particles was distilled in vacuum at a pressure of 65mm and a temperature not exceeding 50 C until 3500 cc of the commercial product had been distilled to a volume of 150 cc.



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Fig. 1.

*Pyrex Distilling Flask*

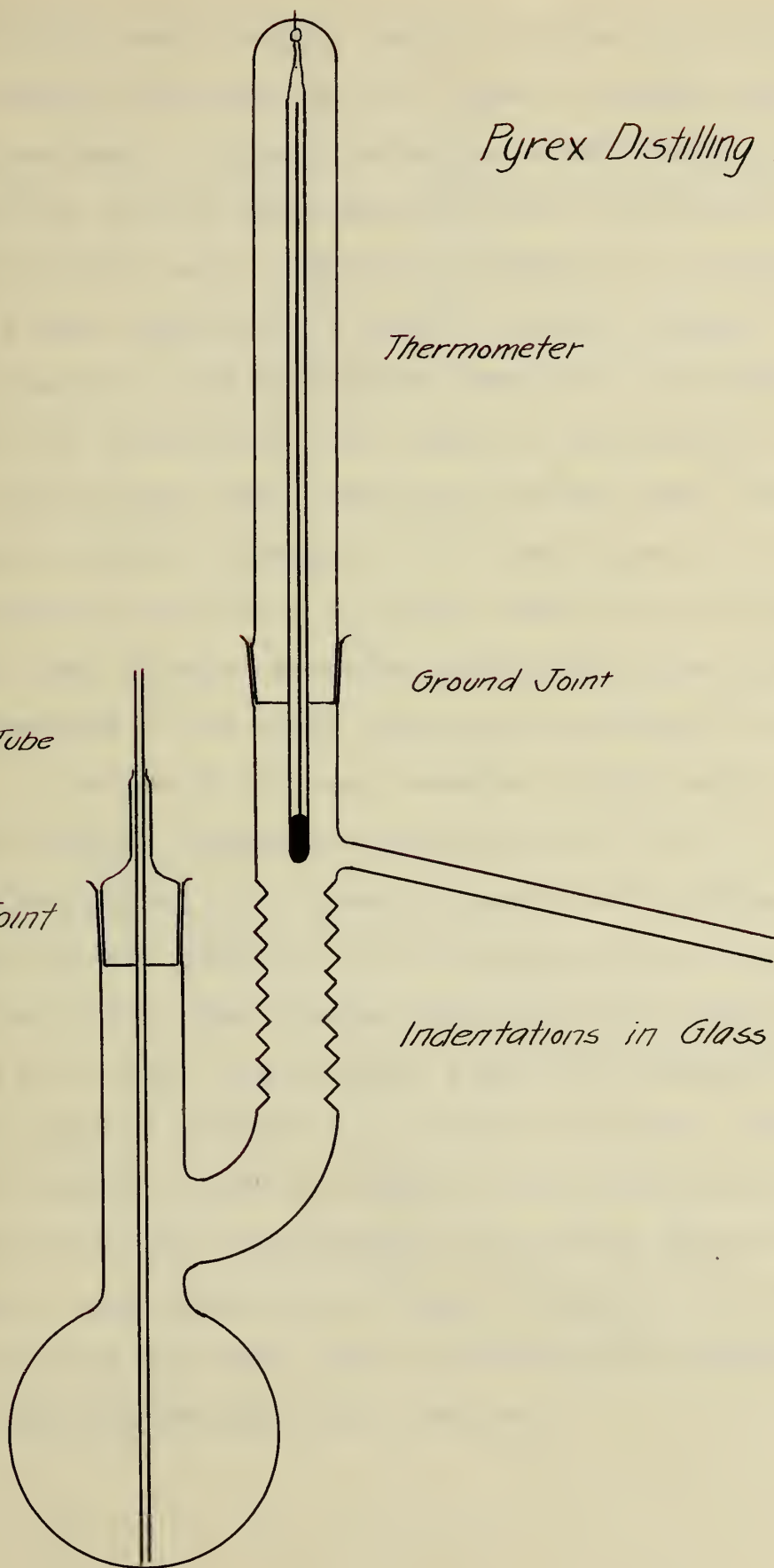
*Thermometer*

*Ground Joint*

*Capillary Tube*

*Ground Joint*

*Indentations in Glass*







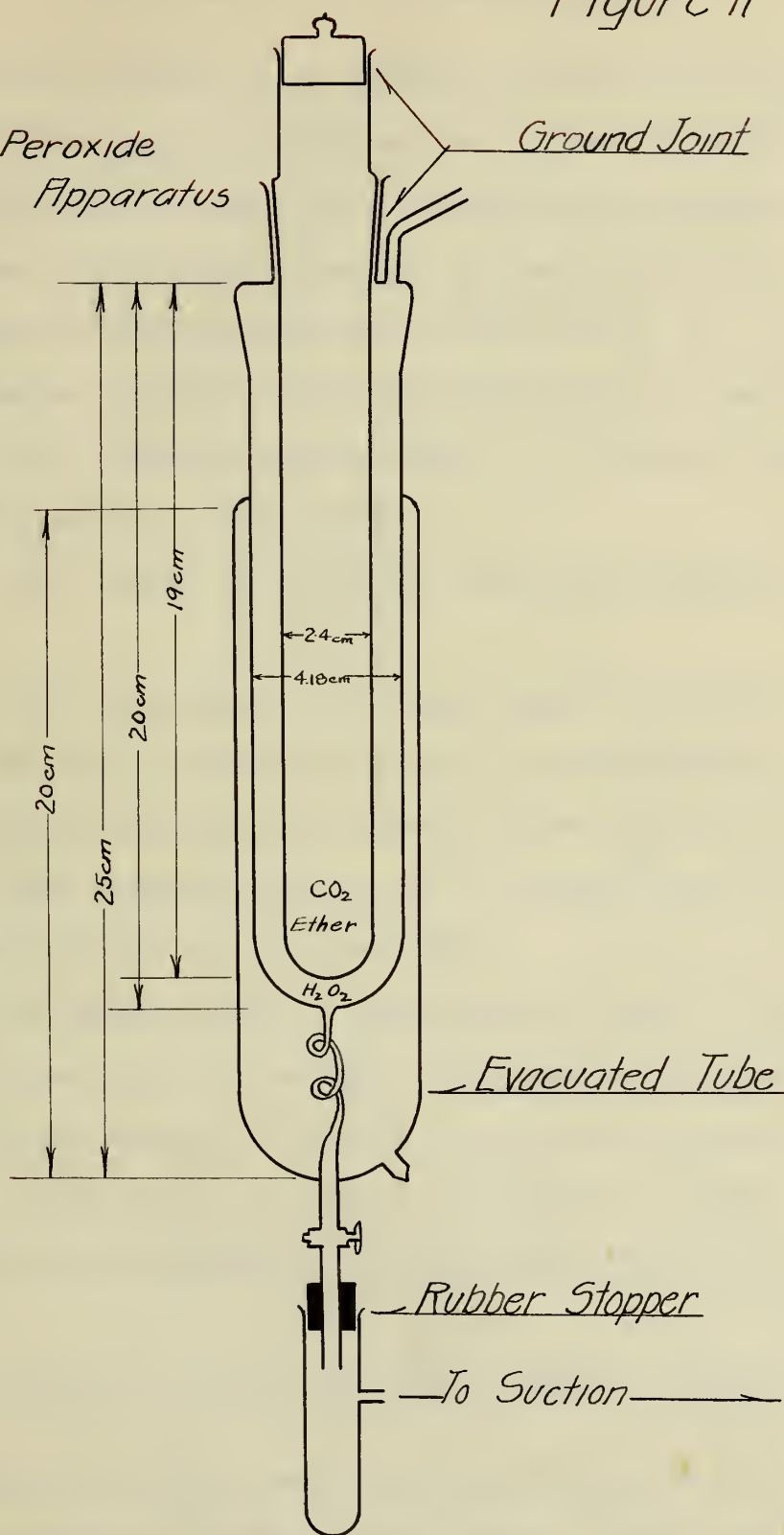
The distillate was rejected. Analysis of the distillate had been made on several occasions and was found to contain only a very small percentage of hydrogen peroxide, a fact which is in accord with the work done by Wolffenstein<sup>13</sup> on the distillation of hydrogen peroxide under diminished pressure. The distilling flask was then replaced by a flask of special design as graphically<sup>shown</sup> in figure (1) and the product completely distilled. The distillate so obtained was free from all solid impurities. This clear distillate was then distilled from the same flask and the fraction boiling between 60 - 75 C was saved. Any distillate which came over below this range was added to the ordinary three per cent hydrogen peroxide. During this final distillation the temperature of the water bath was not allowed to exceed 80 C

A volume of hydrogen peroxide usually amounting to 40 cc and boiling between the temperature of 60 - 75 C at 65 mm pressure was placed in a freezing apparatus of a design as shown in figure (2) and subjected to a cooling mixture of solid carbon dioxide and ether. When further crystallization had ceased, the crystals were freed from adhering liquid by opening the stop-cock and applying suction to an attached receiver. The crystals were now allowed to melt by removing the freezing mixture and substituting slightly warm water in its place. When the crystals had melted, crystallization was again affected as had been previously done and after three crystallization hydrogen peroxide of 99 - 100% concentration was obtained.



Figure II

Hydrogen Peroxide  
Freezing Apparatus







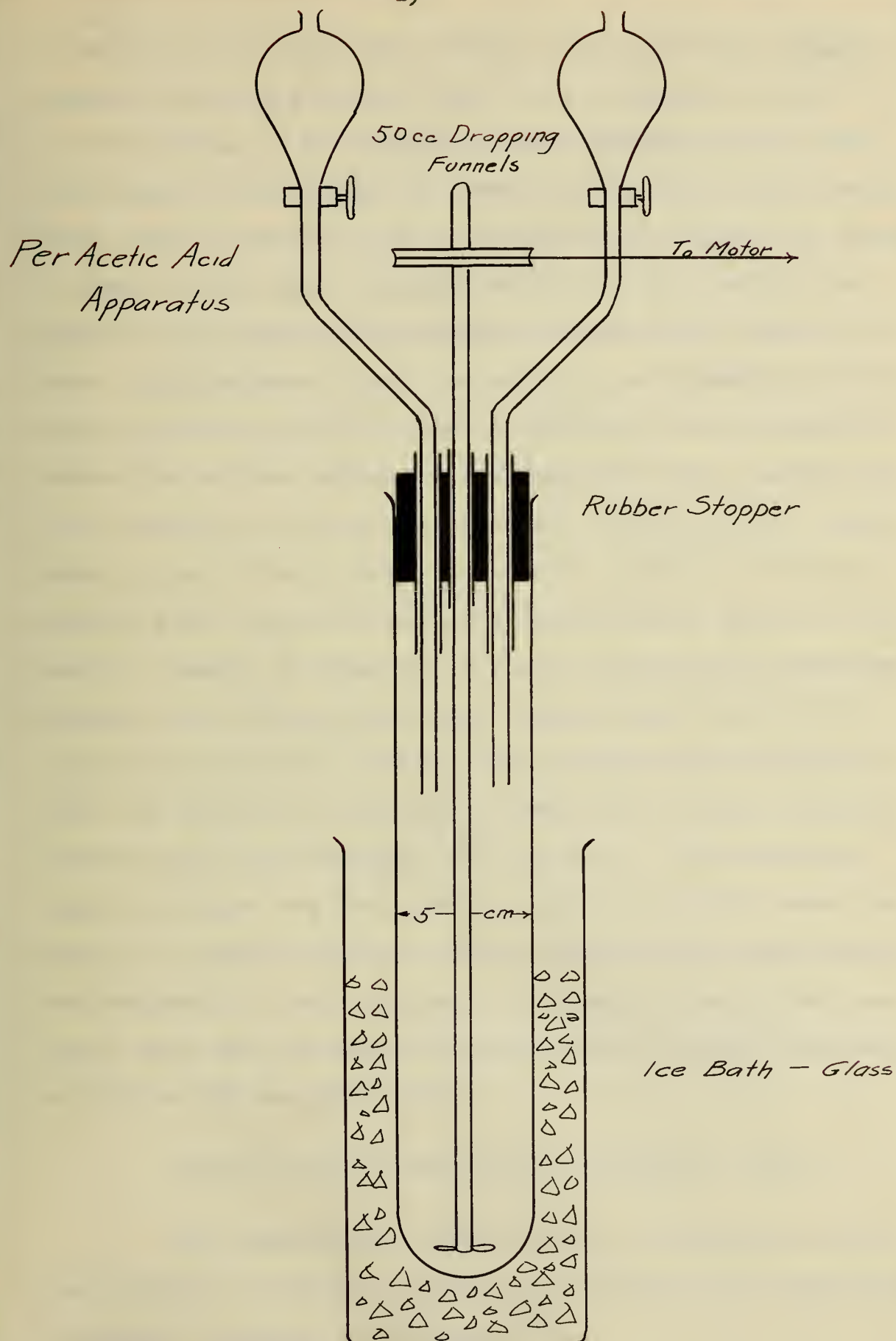
## Preparation of Peracetic Acid.

In the preparation of peracetic acid by the method employed by J.d'Ans and W.Frey<sup>6</sup> in which one mol of acetic anhydride is allowed to react with two mols of hydrogen peroxide in the presence of a catalyst several precautions must be observed otherwise serious explosions may result. It is of utmost importance that the following precautions be taken:

1. The starting reagents must be absolutely pure and free from all traces of solid matter.
- 2/ The vessel in which the reaction is carried must be clean.
3. The substances must react immediately else an accumulation of the products may result in the formation of a violent reaction should the substances once start to react.
4. The solution should not be cooled below + 5 C otherwise the reaction will be retarded.
5. If some peracetic acid solution can be obtained it is best to use this as a catalyst in place of sulphuric acid, which must be used should no peracetic acid be available.
6. Presence of an excess of hydrogen peroxide at all times otherwise an undue amount of diacetylperoxide will be formed.
7. Effective stirring of the reaction mixture.

One mol of acetic anhydride (boiling over 2 C) was placed in a separatory funnel A and 2 mols of 100% hydrogen peroxide in a separatory funnel B (see figure ). The reaction flask was cooled in an ice mixture and into the flask 2 cc of









1% sulfuric acid were added. Should some previously prepared peracetic acid be available then it is advisable to use 2 cc of this instead of the sulphuric acid. Hydrogen peroxide was now allowed to drop into the vessel in slow drops, care being taken that the rate of flow of the hydrogen peroxide was equal to that of the acetic anhydride as in this way the hydrogen peroxide will always be in excess. As soon as the addition of these ingredients was begun, the solution was vigorously rotated with an electric stirrer. After a few cc of the reacting substances had been added, the cooling mixture was removed and the temperature of the solution noted. If the reaction vessel showed signs of heat evolution, then the addition of the ingredients was continued and the cooling mixture applied to the reaction vessel, if however, no signs of heat made themselves manifest the cooling mixture was removed until the initial reaction had started. After all the initial reagents had been added the reaction was allowed to stand for an hour. Vigorous stirring was used throughout the reaction. The complete reaction mixture was then removed from the reaction vessel and placed in a glass stoppered bottle. Samples were then extracted and analyzed for their contents of hydrogen peroxide and peracetic acid. By this method solutions were obtained containing as high as 47% peracetic acid.

#### Quantitative Determination of Peracetic Acid.

The quantitative determination of peracetic acid in the presence of hydrogen peroxide was carried out by employing the method on Baeyer and Villiger.<sup>14</sup>





Two cc of peracetic acid measured out in a pipette was diluted to 100 cc in a volumetric flask and 10 cc of this solution was taken for titration. Ten cc of this solution was diluted to 150 cc and the hydrogen peroxide was titrated with a N/10 potassium permanganate solution. When the end point was reached 3 grams of potassium iodide was added and the liberated iodine titrated with standard sodium thiosulphate using starch as an indicator. The sodium thiosulphate solution used was standardized against a potassium permanganate solution according to the method outlined in Treadwell and Hall

Method used for the Oxidation of Azobenzenes  
to Azoxybenzenes.

The azo body to be oxidized was dissolved in glacial acetic acid, previously warmed to 50 C, and an amount of peracetic acid solution, slightly more than the quantity theoretically required was added. The reaction was then placed on a water bath not exceeding 60 C until the deeply colored solution turned pale in color. At no time did the time required to complete the oxidation exceed one and one-half hours. The oxidized product was then poured into cold water, filtered and dried. Further purification could then be conveniently accomplished either by crystallization from alcohol or petroleum ether.

Oxidation of p-Bromazobenzene.

Twelve grams of p-bromazobenzene in 200 grams of glacial acetic acid was heated on a water bath (50 - 60 C) and



30 cc of 47% peracetic acid solution was added. After one hour the flask was removed and allowed to stand for two hours. The solution was then poured into 1200 cc of cold water and after the precipitate had coagulated, the oxidized product was filtered, washed several times with water and then dried. Twelve grams of orange yellow product melting at 68 - 70.5 C was obtained comprising a yield of 94.5%.

#### Oxidation of p-Ethoxyazobenzene.

Fifteen grams of p-ethoxyazobenzene was dissolved in 200 grams of glacial acetic acid, 21.6 cc of 47% peracetic acid solution added and the mixture heated on a water bath (50-60 C) for one hour. After allowing the oxidized product to stand for several hours, it was poured in to 1200 cc of cold water and when the precipitate had coagulated it was filtered washed and dried. A total yield of 14 grams, comprising a yield of 87% of the theoretical was obtained. The product was ivory yellow in color and melted at 51 - 55 C.

#### Separation of Isomers.

Twelve grams of p-bromazobenzene, ivory yellow in color and melting between 67 - 70.8 C was dissolved in 400 cc of petroleum ether (B.P 30 - 50 C) and the solution filtered. The clear solution was cooled in ice and when no further precipitation took place the crystals so obtained were filtered off and the filtrate evaporated to a volume of 300 cc . The solution was again cooled, the crystals separated and the remaining solution evaporated to 200 cc . The cooling process







was then repeated, the crystals removed and the filtrate allowed to spontaneously evaporate to dryness. The following fractions were obtained:

No.	Grams	color	M.P.
Aa	2.70	Ivory yellow	80 - 84 C
Bb	3.10	Ivory yellow	66 - 68 C
Cc	2.00	Ivory yellow	65 - 68 C
Dd	2.10	Slightly orange	63 - 64 C

#### Crystallization of the Separate Fractions.

The fraction Aa and the combined fractions Bb and Cc were recrystallized from 125 cc petroleum ether (30 - 50 C) by the same method as previously outlined. The fraction Dd was dissolved in glacial acetic and reoxidized with the peracetic acid solution. The fraction of Dd reoxidized consisted of 200 grams of a light ivory yellow product of melting point 63 - 64 C. The following fractions were obtained:

No	Grams	Color	M. P.
Aa.1	3/4	Ivory yellow	92 - 93 C
Aa.2	3/4	Ivory yellow	91 - 92.5 C
Aa.3	1/2	Ivory yellow	86 - 87 C
Bb-Cc.1	1.8	Ivory yellow	68 - 70 C
Bb-Cc.2	1.5	Ivory yellow	66 - 68 C
Bb-Cc.3		Ivory yellow	65 - 66 C
Bb-Cc.4		Ivory yellow	65 - 66 C
Dd.1		Ivory yellow	63.5 - 65.6 C
Dd.2		Ivory yellow	63 - 64.6 C
Dd.3		Ivory yellow	63 - 65 C



The fraction Aa.1 was then reoxidized and a product which melted over the same range as the starting material was obtained. On recrystallization from 40 cc of petroleum ether ivory yellow plates of melting point 94.4 - 95.4 C were obtained. This product corresponded in all respects with the isomers obtained by Angeli.

The fraction Bb-Cc.1 in acetic acid solution was then reoxidized with peracetic acid and recrystallized from petroleum ether. The fraction of the following constants were obtained:

No	Grams	Color	M.P.
Bb-Cc.1a	0.5	Ivory yellow	71 - 73 C
Bb-Cc.1b	0.5	Ivory yellow	65 - 68 C
Bb-Cc.1c	trace	Ivory yellow	64 - 66.4 C.

Fractions Bb-Cc.2 and Bb-Cc.3 were recrystallized from petroleum ether in the same manner as previously carried out. Fractions of the following constants were obtained.

No	Grams	Color	M.P.
Bb-Cc.2a	trace	Ivory yellow	70 - 73 C
Bb-Cc.2b	0.4	Ivory yellow	65 - 68 C
Bb-Cc.3a	trace	Ivory yellow	64.8 - 67 C
Bb-Cc.3b		Ivory yellow	65 - 68 C
Bb-Cc.3c	0.2	Ivory yellow	65 - 67 C

To obviate any possibility of the fractions as separated to be mixtures of unoxidized azo and azoxybenzenes a second series of recrystallizations were carried out in which each of the separated fractions were again subjected to the oxidation. Crystallization of the reoxidized products were then





affected in a manner identical in all details with the initial recrystallizations.

### Second Series of Recrystallizations.

The oxidation products from 12 grams of p-bromazobenzene were crystallized from 400 cc of petroleum ether (30 -50) using the system outlined in the first crystallization and the following fractions were obtained:

No.	Grams	Color	M.P.
A	2.1	Ivory yellow	79 - 80.5 C
B	2.6	Orange yellow	68 - 69.5 C
C	1.1	Orange yellow	66 - 67.5 C
D(residue)	3.1	Orange red	64 - 67 C

The fractions obtained from the crude oxidized product were further fractionated as tabulated below.

No.	Grams	Color	M.P.
A.1	0.50	Ivory yellow	92 - 93.5 C
A.2	0.40	Ivory yellow	91 - 92.5 C
A.3	0.15	Ivory yellow	85 - 85.5 C
A.4	0.70	Orange	69 - 71.5 C
B.1	0.30	Ivory yellow	79 - 80.5 C
B.2	0.60	Ivory yellow (darker	67 - 68 C
B.3	1.10	Orange	64.5 - 67.5 C
C.1	0.7	Ivory yellow	80 - 84 C
C.2	trace	Ivory yellow	68 - 71.8 C
C.3	0.80	Orange	





The fraction D was dissolved in glacial acetic acid and oxidized with 10 cc of peracetic acid solution 45.6%. After allowing to stand over night, the solution was again treated with peracetic acid and the oxidation completed on the water bath. The reaction mixture was poured in to water, filtered and dried. Crystallization yealded the following fractions:

No.	Grams	Color	M.P.
D.1	0.40	Ivory yellow	66 - 68.8 C
D.2	0.40	Ivory yellow	66 - 68 C
D.3	0.10	Ivory yellow	65.5 - 67.5 C

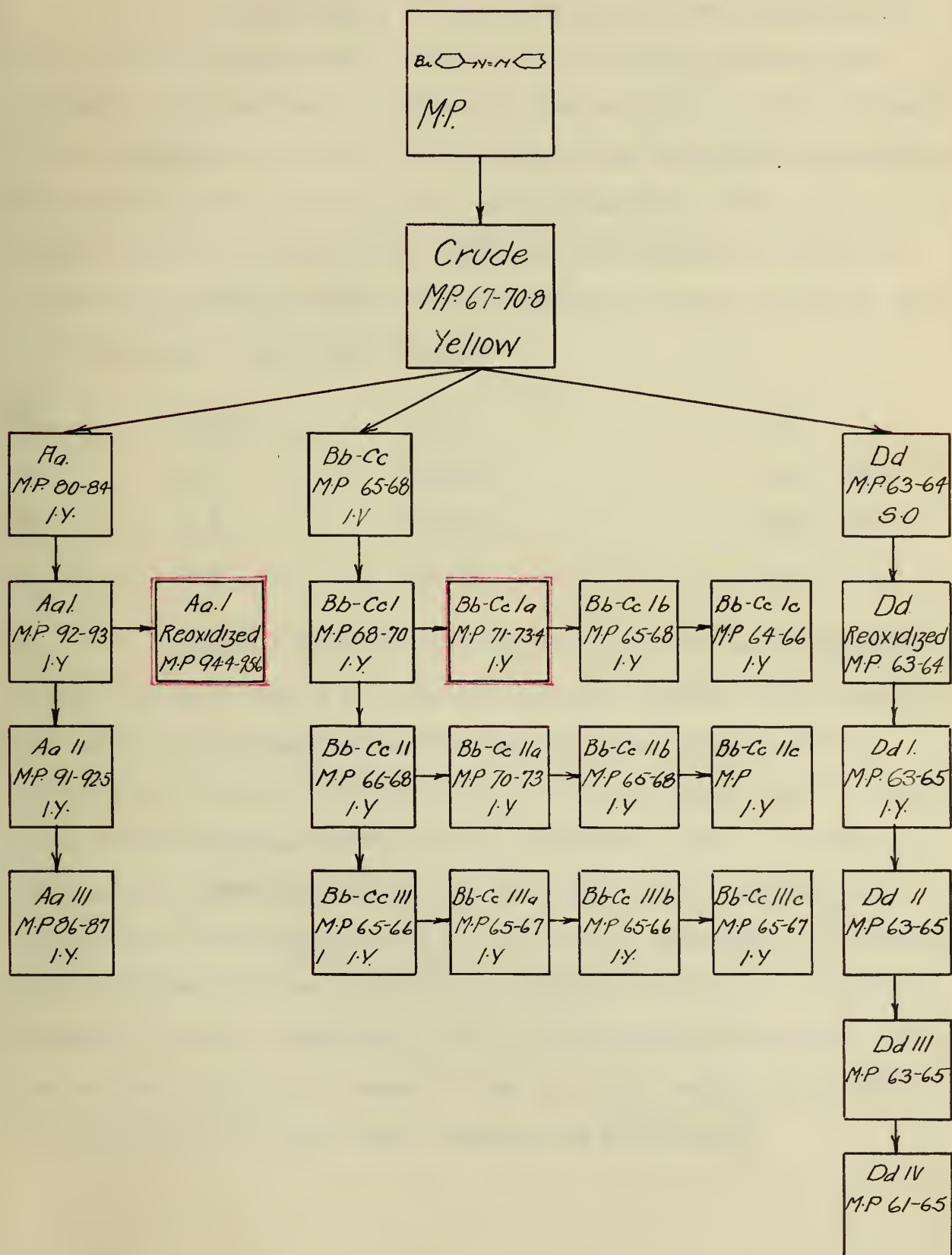
The fractions A1,A2, A3, A4, B1, B2, B3, C1, C2, and C3 were each placed in a separated test tube, 10 cc of glacial acetic acid and 3 cc of peracetic acid was added. After the oxidation reactions showed no further decrease in the color intensity they were poured into water and the precipitate filtered and washed. The melting points of the crude products were:

A.1- 91.6 - 93.4 C.	B.1-	C.1- 80 - 82 C.
A.2- 84 - 85 C.	B.2- 65.5 - 68 C.	C.2- 69 - 71 C.
A.3- 84 - 85 C.	B.3- 64 - 66 C.	C.3-
A.4- 68 - 70.6 C.		

The reoxidized fractions A4, B2, abd B3 were mixed together and the total mixture placed in a test tube and re-crystallized from petroleum. The fractions obtained were:

F.1	M.P.	Color	
F.1	67 - 70 C	Light yellow flakes	60 Grams
F.2	67 - 68 C	Light yellow flakes	40 Grams



Crystallization of *p*-Brom-Azoxybenzene





## Separation of Isomers of p-Ethoxy-azoxybenzene.

Thirteen grams of oxidized product was dissolved in 400 cc of petroleum ether (B.P. 30 - 50 C) and the solution filtered with suction. By allowing the solution to cool in water of a temperature of 24 C, fine needle-like crystals were obtained. The crystals were filtered off and the solution evaporated until three-fourths of the volume remained. On cooling further crystallization took place. This process was further continued and the following fractions obtained:

No.	Grams	Color	M.P.
A	2.6	Yellow	61 - 68 C
B	2.8	Yellow	55 - 58 C
C	4.4	Yellow	53 - 54 C

These fractions were again reoxidized and recrystallized. In this series of crystallizations accurate data as in the case of p-brom-azoxybenzene had not been taken but the individual fractions obtained were recrystallized until no further rise in the melting points of the fractions could be obtained. By repeated crystallizations it was possible to separate two compounds, one melting at 72 C, and called by Angeli ( ) isomer, and the other melting at 55 56 C designated as the ( ) isomer. However a product melting at 50 - 51 C was obtained which had properties similar to those of the 55 - 56 C melting substance. Further work to check these isomers was undertaken.



The results of the complete series of separations shows that of those fractions which were obtained and which are to be regarded as isomeric forms of p-bromazoxybenzene, are free from any unoxidized azobenzenes since no variation in the melting point had been noticed. Furthur they substantiate the fact that the melting point of the higher melting isomer is 94 - 94 C and that there is a possibility of the existance of two compounds, one melting in the neighborhood of 65 - 66 C and the other one 72 - 73 C one of which may be an isomer, whereas the other may be a mixture of the high melting isomer and the low melting isomer. The one which can really be considered an isomer is questionable since all attempts to convert the compound melting at 94 - 95 C, or vica versa, were unsuccessful. Had such a procedure been successful then it would have bee possible to alter the melting point of either the 65 C or the 72 C melting substance if one of these is to be looked upon as a mixture of the high and low melting isomers.

It should be mentioned at this point that the melting points of the substance were determined with a 50 - 100 C AnschUz Thermometer, the total stem of the thermometer being immersed in the cotton seed oil. The melting points in each case were taken several times in order to avoid any possibility of error.





## Discussion of Results.

The work herein presented gives an indication in only a small way of the possibilities of peracetic acid as an oxidation agent for unsaturated organic compounds. It shows that ~~that~~ the reagent has the following advantages:

1. A very rapid oxidizing agent.
2. Simplicity of procedure and ease of separation of the oxidation products.
3. Cleanliness of reaction products in that no foreign impurities which can not be easily removed are present.

The results of the oxidation of the unsymmetrical azobenzene shows that there are different products resulting from such oxidations and in view of the fact that the substances can not be considered as mixtures of the oxidized and unoxidized azobenzenes because of the completeness of the oxidation one is led to believe that these isomers do actually exist. There are, however, minor differences in which the author does not agree with Angeli, the following in particular. In case of the p-bromazoxybenzene the melting point was found to be identical with that found by Angeli. However, for the lower isomer the results are not as concordant. A substance melting at 72 - 73 C was obtained and an addition compound melting at 65 - 66 C was found. In the case of the p-ethazoxybenzene the same was true. A substance melting at 50 - 51 C, and one melting at 55 - 56 C are called by Angeli the *B* form and a substance melting at 71 - 72 C called the *α* form. Now which of these of these sub-





low melting substances is an isomer and what can the other be considered as. The author is not able to answer this in view of the following: the 72 - 73 C melting isomer may be a mixture of the 94 C and 66 C melting substances, or the 66 C may be a mixture of the 94 C and the 72 C melting substances. (See chart 4) The same could be true of the p-ethoxy-azoxybenzene.



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